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Thesis

THE LIQUEFACTION AND SOLIDIFICATION OF GASES

Submitted by

Harold Kent Ireland

(S.B., Boston University, 1924)

In partial fulfilment of requirements for

the degree of Master of Arts

1928

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OUTLINE

THE LIQUEFACTION AND SOLIDIFICATION OF GASES

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PART I

THE MORE IMPORTANT STEPS IN THE HISTORY OF THE EXPERIMENTAL LIQUEFACTION AND SOLIDIFICATION OF GASES

1. Anticipatory Suggestion by Lavoisier 1784

Although several scientific investigators prior to Lavoisier, of whom we may consider Van Helmont and Boerhaave as outstanding examples, appreciated the possibility of condensing gases, none expressed their conjectures so admirably as did Lavoisier when he wrote in 1784, "Consider for a moment what would happen to the different substances which compose the globe if its temperature be suddenly changed. Suppose for instance that the earth . . . should be suddenly placed in a very cold region . . . the water which at present forms our rivers and seas, and probably a majority of the liquids which are known would be transformed into solid mountains. On this supposition the air, or at least a part of the aeriform substances which compose it, would doubtless cease to exist in the state of an invisible fluid, for want of a sufficient degree of heat; it would return to the liquid state, and this change would produce new liquids of which we have no knowledge."*

2. Early Experimenters

Monget and Clouet**are generally credited with condensing, before 1800, sulphurous acid gas in a U tube surrounded by a mixture of ice and salt by the application of "strong pressure" and "intense cold". The temperature thus obtained could not have been much lower than -18 degrees centigrade.

By experiments on the elasticity of gases Dalton was led to the following conclusions which he gave in his essay, "On the Force of

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* Lavoisier, Oeuvres, ii,805

** Accum's Chemistry, I, p.345

Steam or Vapour from Water and various other Liquids", in 1801. "There can scarcely be a doubt entertained respecting the reducibility of all elastic fluids of what-ever kind into liquids; and we ought not to despair of effecting it in low temperatures and by strong pressures exerted on the unmixed gases."

In connection with experiments primarily chemical, Northmore* in 1805 liquefied chlorine by compression, obtaining a yellow, extremely volatile liquid. In a similar way he condensed hydrochloric acid gas and sulphurous acid gas but failed with carbonic acid gas. Unfortunately these experiments aroused little if any interest, and consequently did not advance the development of the liquefaction of gases.

3. Experiments of la Tour 1822

By heating liquids in sealed glass tubes Cagnaird de la Tour** in 1822 gained some instructive ideas concerning the relations between the liquid and the gaseous states. He pointed out that alcohol, naptha and ether on being subjected to heat and to pressure vaporized completely in a space not much greater than that occupied by the liquid alone, and that the liquid always disappeared at the same temperature. He formulated this hypothesis, "There is for every vaporizable liquid a certain temperature and pressure at which it may be converted into the aeriform state in the same space occupied by the liquid."***

In general, scientists did not realize the importance of la Tour's work although Faraday evidently found it suggestive.

4. Early Work of Faraday 1823

In 1823, Faraday**** accidentally liquefied chlorine by cooling it

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* Faraday, Liquefaction of Gases, p.28
** Hardin, Liquefaction etc., p.18
*** Sloane, Liquid Air, p.20
**** Faraday, Liquefaction of Gases, pp.1-33

in a closed bent glass tube where it had been produced under pressure by the moderate heating of hydrate of chlorine. Quick to appreciate the significance of the accomplishment he confirmed the result by subjecting dry chlorine gas to pressure, and then extended his experiments to other common gases. In speaking of the chlorine experiment he said, "Chlorine had been entirely separated from the water by the heat and condensed into a dry liquid by the mere pressure of its own abundant vapour!"*

About this time Davy had liquefied hydrochloric acid gas by a similar process and had suggested its application to other gases.** At his suggestion Faraday continued the work alone, succeeding in condensing sulphurous acid, sulphuretted hydrogen, carbonic acid, nitrous oxide, euchlorine, cyanogen and ammonia before other matters claimed his attention. The fact that he had been unable to liquefy such gases as oxygen, hydrogen and nitrogen kept alive his interest and led him to take up the research again, twenty-one years later, as will be related.

5. Work of Thilorier 1834

Thilorier*** produced carbon dioxide gas by chemical action in a strong wrought-iron container, the resulting pressure causing some of the gas to liquefy in a connected wrought-iron receiver. The yield of liquid dioxide was greatly increased by surrounding the receiver with a freezing mixture. The generator could be cut off from the receiver, recharged and more carbon dioxide gas passed into the receiver for condensation. In this way as much as two or three liters of the liquid could be collected.

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* Alembic Club Reprint, #12, p.86
** Ibid., p.88
*** Hardin, Liquefaction etc., p.33

Thilorier studied the physical properties of liquid carbon dioxide. He discovered that ether mixed with liquid carbon dioxide was useful in producing low temperatures. By allowing liquid carbon dioxide to expand suddenly, he found that a white solid was formed which proved to be solid carbon dioxide. This mixed with ether gave the then remarkably low temperature of -110 degrees centigrade, and became known as "Thilorier's Mixture".

6. Work of Natterer 1844

Natterer* made use of a hand-operated reciprocating type of compression pump of high mechanical advantage taking gas from a receiver and delivering it highly compressed to a strong wrought-iron tank surrounded by a freezing mixture. He liquefied and solidified carbon dioxide and nitrous oxide but although he used pressures as high as 3600 atmospheres he was unable at ordinary temperatures to effect the liquefaction of such gases as carbon monoxide, air, oxygen and hydrogen. Realizing that high pressure alone was insufficient for the liquefaction of such gases, he cooled the compressed gases with Thilorier's Mixture, but without success as the temperature was not low enough.

7. Later Work of Faraday 1845

In 1845, his enthusiasm fired by the experiments of Thilorier, Faraday again attacked the problem of liquefaction of gases "in hope of seeing oxygen and hydrogen either as liquid or solid bodies, and the latter probably as a metal".** He used a two-stage compression pump forcing the gas into small-diameter condensing tubes of green bottle glass having U shaped bends which could be cooled readily in Thilorier's Mixture, which under exhaustion gave a temperature of -166 degrees Fahrenheit. Treating them in this way, under pressures up to 50

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* Ibid., p.56

** Faraday, Experimental Researches, p.96

atmospheres, Faraday caused to liquefy the following gases: olefiant, hydriodic acid, hydrobromic acid, fluosilicon, phosphuretted hydrogen, fluoboron and muriatic acid; and caused to solidify: hydriodic, hydrobromic, sulphurous and carbonic acids, hydrogen sulphide, euchlorine, nitrous oxide, cyanogen and ammonia.* In accounting for the fact that even at -166 degrees Fahrenheit there were no signs of condensation for hydrogen, oxygen, nitrogen, nitric oxide, carbon monoxide and coal gas, Faraday suggested that -166 degrees Fahrenheit for these gases is above the temperature at which they assume the Cagniard de la Tour condition of vapour and liquid having the same density. He concluded that "further diminution of temperature and improved apparatus for pressure may well be expected to give us these bodies (nitrogen and hydrogen) in the liquid or solid state."

In reviewing his work Faraday stated, "I have added to the list of those that could previously be shown in the liquid state, and have reduced seven including ammonia, nitrous oxide and sulphuretted hydrogen into the solid forms."**

8. Work of Berthelot 1850

Berthelot***confined the gas to be compressed in a capillary portion of a thick-walled sealed glass tube otherwise filled with mercury. On heating the mercury it expanded more than did the glass and produced very high yet safe pressures on the confined gas. He condensed such gases as chlorine, ammonia and carbonic acid but failed with nitric oxide, carbon monoxide and oxygen, although he used solid carbon dioxide for cooling the latter gas.

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* Faraday, Liquefaction of Gases, pp.19-68

** Faraday, Experimental Researches, p.124

*** Hardin, Liquefaction etc., p.61

9. Experiments of Andrews 1863

Although Andrews* did not add to the list of gases previously liquefied, his experiments with carbon dioxide were of great theoretical value. He confined the gase above a mercury plunger in a strong calibrated capillary tube of glass closed at the top, the bottom being placed in a strong copper tube filled with water and equipped with a screw plunger for applying pressure to the water, and thereby to the gas. Investigating the relations of pressure, temperature and volume, and those of gas and liquid very thoroughly, Andrews found that carbon dioxide could not be liquefied above a certain temperature (30.92 degrees centigrade) no matter how great the applied pressure. He had found the critical temperature of carbon dioxide.

Andrews extended his investigations to other common gases and found that each had a critical temperature. In no case did he find an abrupt change in the physical properties as the gas passed through the critical point. Referring to this phenomenon he wrote, "From carbonic acid as a perfect gas to carbonic acid as a perfect liquid, the transition . . . may be accomplished by a continuous process and the gas and liquid are only distant stages of a long series of continuous physical changes."

10. Work of Cailletet 1877

Cailletet's apparatus** consisted of a small but strong glass tube closed at the upper end, with gas above and mercury below, the lower part of the tube being held in an iron well partly filled with mercury having provision for the entrance of water under high pressure from a pump. The gas-filled portion of the glass tube was surrounded by a

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* Trans. Roy. Soc. 1869, part 2, p.575; 1876, part 2, p.421

** Hardin, Liquefaction etc., p.115

low-temperature bath of liquid nitrous oxide. After compressing the gas strongly, and waiting long enough for the heat of compression to be removed by the cooling bath, the pressure was suddenly released and the gas cooled itself greatly by expansion. If condensation occurred, drops of liquid were visible in the tube. Among others of the less difficult gases Cailletet condensed acetylene, nitric oxide and methane. He also condensed in a similar fashion oxygen, carbon monoxide, nitrogen and air. He thought that he succeeded with hydrogen, but he probably failed. In no case could he obtain more than very minute and transient amounts of liquid gases.

11. Work of Pictet 1877

Pictet* thought that if the temperature of gases under high pressure could be sufficiently reduced the molecular cohesion of the gases would condense them to liquids or solids, so he devised apparatus with special attention to the matter of cooling the compressed gases.

In the case of oxygen liquefaction, the apparatus consisted of three related stages. A compression pump circulated sulphurous acid, which vaporized in a chamber surrounding the condensation tube of a similar circuit of carbonic acid or protoxide of nitrogen, thereby cooling the latter gas enough to effect condensation under pressure, this liquid in turn vaporizing in a chamber surrounding the condensation tube of an oxygen circuit. The oxygen gas under a pressure of several hundred atmospheres was produced by heating a mixture of potassium chlorate and potassium chloride in a strong wrought-iron flask connected to the condensation tube. Some idea of the care with which Pictet worked can be gained from the fact that, before attempting the experiment proper, he spent fifteen days in testing the apparatus and in

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* Ewing, Mechanical Production of Cold, p.135

determining the optimum conditions of operation. In this experiment, which lasted four hours, he succeeded in momentarily liquefying and probably in solidifying oxygen by the sudden release of pressure upon the highly compressed and cooled gas. Using a similar apparatus with hydrogen he also liquefied it as a mist, and probably solidified it in minute amounts.

12. Work of Hautefeuille and Chappuis 1882

These investigators by compressing ozone in a Cailletet apparatus and by utilizing the low temperature given by a jet of liquid ethylene obtained ozone in the liquid state.*

13. Work of Wroblewski and Olszewski 1883

These experimenters confined the gas to be investigated in a large glass tube within a very strong iron cylinder which could be flooded with mercury, thereby forcing the gas into a small but strong glass tube outside the cylinder. A chamber in which cooled liquid ethylene could be evaporated under pressure surrounded the condensation tube. With this apparatus, said to be capable of withstanding internal pressures of 500 atmospheres, the co-investigators liquefied oxygen, nitrogen and carbon monoxide.

Employing a somewhat more complicated apparatus and using rapidly evaporating liquid gases under reduced pressure as refrigerants, Wroblewski was able to liquefy hydrogen, oxygen, air, nitrogen, carbon monoxide and methane. He pointed out the fact that the use of very low temperatures permitted liquefaction of most gases at moderate pressures.

By evaporating the liquid gases under greatly reduced pressure

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* Hardin, Liquefaction etc., p.137

Olszewski was able to solidify: carbon monoxide, nitrogen, methane, nitric oxide, chlorine, hydrochloric acid, hydrofluoric acid, phosphine, arsine, stibine, ethylene, silicon tetrafluoride and hydrogen selenide.

14.Work of Linde on Air 1895

Although Linde was more an inventor than an investigator, his contribution to the science of liquefaction of gases is decidedly important for the reasons that his process is continuous and that it produces the liquefied gases in large quantities.

In Linde's apparatus* the air to be liquefied is compressed to about 200 atmospheres, and is cooled by water to remove the heat of compression. The cool compressed air passes through the inner tube of a system of concentric spiral metal tubes and issues through an expansion valve into a receiver, the air being somewhat cooled by self-expansion. This cold air on its way back to the compressor passes out of the receiver by the outer spiral tube, thereby cooling the air flowing toward the receiver in the inner tube, which air presently expands becoming still colder. As the process continues the temperature of the air entering the receiver falls until the air begins to liquefy.

For operation, liquefying devices of the type require merely supplies of gas and of engine power, reducing the gas to a liquid without the use of complicated auxiliary cooling devices.

15.Work of Dewar on Oxygen, on Nitrogen and on Air 1895-9

Dewar**began his work on the liquefaction of gases about 1880, determining their critical constants. Somewhat later, he constructed

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* Ewing, Dictionary of Applied Physics, p.568

** Dewar, "Liquid gases", Encyclopaedia Britannica, 12th Edition

an apparatus for the lecture-room demonstration of the liquefaction of oxygen on a small scale. In 1886 he devised an apparatus for producing liquid gases in considerable quantity. In these machines liquefaction was brought about by subjecting the highly compressed gases to intense cooling by auxiliary refrigerants. In 1892 Dewar succeeded in freezing liquid air into a clear transparent ice. In 1893 he devised the vacuum flask for storing liquid gases.

In 1895 he applied the principle of refrigeration by self-intensification to the construction of a compact apparatus for liquefying air, oxygen etc. The gas under a pressure of about 150 atmospheres is cooled by liquid carbon dioxide, and is then allowed to expand from a regenerative coil into a vacuum vessel, being further cooled by self-expansion. This cold gas passes around the regenerative coil lowering the temperature of the compressed gas within, approaching the expansion valve. Within fifteen minutes after starting the device, liquid gas begins to drop from the expansion valve. This apparatus gave Dewar the means of obtaining liquid gases in considerable amounts.

In 1897 Moissan and Dewar liquefied fluorine for the first time. The gas condensed but did not solidify at the temperature produced by evaporating liquid oxygen or liquid air under reduced pressure.
In 1898 Dewar obtained liquid hydrogen in considerable quantity for the first time by self-expansion of the highly compressed and intensely cold gas.

16. Work of Olszewski on Argon 1895

In 1895 Olszewski* subjected highly compressed argon to low temperatures, using a modified Cailletet type apparatus employing liquid

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* Hardin, Liquefaction etc., p.123

ethylene boiling under reduced pressure as the refrigerant. The argon became liquid, and its critical temperature was found to be about -121 degrees centigrade. The liquid congealed at about -190 degrees centigrade. In a similar way Olszewski strove to liquefy helium but failed. He wrote, "In every single instance I have obtained negative results and, as far as my experiments go, helium remains a permanent gas and apparently much more difficult to liquefy than even hydrogen."

17. Work of Ramsay and Travers on Neon, Krypton and Xenon 1898

By subjecting neon, krypton and xenon to the very low temperatures obtained by evaporating rapidly under low pressure, liquid air or liquid hydrogen, Ramsay and Travers* were able to liquefy and even to solidify these rare gases of the atmosphere; but helium remained gaseous under such conditions.

18. Work of Rutherford and Soddy, also that of Whytlaw-Gray and Ramsay, on Emanations 1902

By means of the low temperature produced by liquid air Rutherford and Soddy condensed thorium emanation.** In a similar way Whytlaw-Gray and Ramsay***liquefied and solidified niton, (radium emanation).

19. Work of Kamerlingh-Onnes on Helium 1908

In 1908 Kamerlingh-Onnes****at the Cryogenic Laboratory at Leyden liquefied helium, because of its very low critical temperature the most difficult of all the gases to condense. He employed the unbalanced-

* Ramsay, Gases of the Atmosphere, pp.228-270
** Travers, Rare Gases of the Atmosphere, p.85
*** Ramsay, Gases of the Atmosphere, p.261
**** Encyclopaedia Britannica, 12 Ed. Vol. 31, p.1175

expansion method of producing low temperatures, allowing the compressed, precooled helium gas to expand and cool regeneratively. At the critical temperature (-268 degrees centigrade) the pressure required to cause condensation of the gas was a little over two atmospheres. Onnes did not succeed in solidifying helium.

20. Work of Keesom on the Solidification of Helium 1926

Keesom had worked with Onnes and, after his death, continued the work on helium. In 1926 he succeeded in solidifying that gas.* By means of a hydraulic press, helium was compressed in a glass tube surrounded by liquid helium boiling under reduced pressure in a Dewar double-walled vacuum vessel, in turn surrounded by a similar concentric vessel filled with liquid hydrogen, similarly surrounded by a vacuum vessel containing liquid air. At a temperature of 4.2 degrees absolute the pressure required to solidify helium was 140 atmospheres, but at 1.1 degrees absolute the pressure required was only 25 atmospheres. The solid helium appeared as a homogeneous transparent mass.

With the solidification of helium by Keesom, all known gases have been liquefied and solidified.

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* Keesom, Science and Invention, Nov. 1926, p.593

PART II

THEORY AND PRACTICE IN THE LIQUEFACTION AND SOLIDIFICATION OF GASES

1. Characteristics of the States of Matter

Matter may be classified as occurring in two general forms, solid and fluid. Solid matter is defined as matter which does not flow of itself, whereas fluid matter does. Fluid matter includes both liquids and gases, the latter being highly compressible but the former practically incompressible. In this classification the term, gases, includes not only the "true gases" but also vapours; the "true gases" being above their respective critical temperatures, and the vapours being below theirs.

Sir Oliver Lodge sets up the following differentia for the states of matter: "A solid has (definite) volume and (definite) shape; a liquid has (definite) volume but no (definite) shape; a gas has neither (definite) volume nor (definite) shape." There is little difficulty in distinguishing between the solid and the liquid states, but the dividing line between the liquid and the gaseous states is not so well marked. Edser* points out that "the only really essential difference between a liquid and a gas is that the former has a definite surface exhibiting the ordinary curved form due to surface tension." If a liquid be warmed ever so slightly above the critical temperature this meniscus disappears, although no change in density need take place.

Jeans** states that the three states of matter are associated with three different types or intensities of molecular motion. If the molecules are quiet at the position of equilibrium, the solid is at the absolute zero of temperature. Any increase of temperature is accompanied

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* Edser, Heat, p.207

** Jeans, Dynamical Theory of Gases, p.2

by a vibratory motion of small magnitude of the molecules about the equilibrium position. As the temperature increases, the molecules become possessed of sufficient kinetic energy partially to overcome the attractions of neighboring molecules; thus they can slip from position, and the material becomes plastic or liquid. In this state, molecules may slip from orbit to orbit readily; which, however, happens less readily in a solid, occurring only when a molecule infrequently acquires supernormal kinetic energy. In gases the kinetic energy of molecules causes them to fill all available space and to exert pressure. Jeans accounts for the near incompressibility of solids and liquids by postulating that the force between molecules changes from attraction at ordinary distances to repulsion at very small distances.

Travers* speaks of the gaseous state as mostly space sprinkled with innumerable molecules in such constant and erratic motion that they can not stay grouped. As the gas is cooled the movements of the molecules diminish and transient clusters form, the molecules within them vibrating violently. Some of the molecules form a sheathing over the wall of the containing vessel by adhesion. With further cooling this sheath thickens, the clots increase; and still further cooling causes all the molecules to form a liquid mass. The molecules are still in violent motion, some escape into the air, some return. With further cooling the oscillations of the molecules become quieter; crystals start to form; doing so well, if the cooling be slow; if it be fast, a glass or jelly is formed. Within the solid the molecules still quiver or vibrate as long as the temperature is at all above the absolute zero (-273.1 degrees centigrade).

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* Travers, The Rare Gases of the Atmosphere, p.86

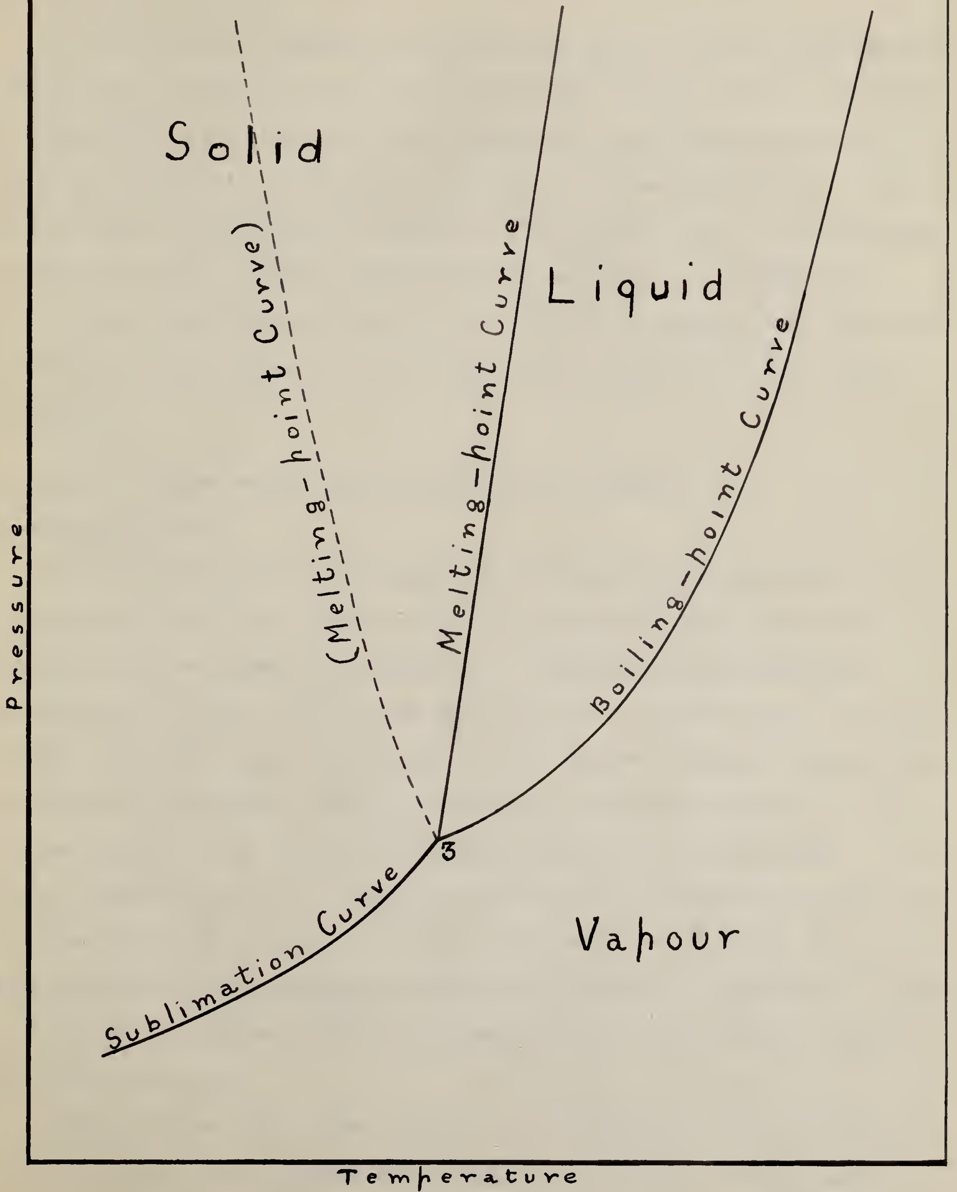
2. Pressure - Temperature Relations for the States of Matter

Even before the experimental study of the liquefaction and solidification of gases, it was suspected by some scientists that any substance could occur as solid, liquid and gas; and, accordingly, that it was possible to change gases into the liquid and solid forms by suitably regulating the conditions of pressure and temperature. With the solidification of helium by Keesom, which completed the reduction of all known gases through the liquid to the solid state, this supposition has been substantiated. Particularly because much of the experimental work overemphasized the importance of the pressure factor, it is desirable for us to consider the temperature - pressure relations for the different phases of a substance.

A curve such as the "melting-point" curve in Fig. 1 may be drawn to represent the relation between temperatures and pressures at which the solid and liquid forms of a substance can exist in equilibrium, all points above the curve corresponding to the existence in the container of liquid only, and all points below the curve to the existence of solid only. Similarly a "boiling-point" curve will represent the temperature - pressure relations of liquid and vapour in equilibrium, all points above the curve corresponding to the existence of liquid only, and all points below the curve to the existence of vapour only. In like fashion the state of equilibrium between solid and vapour may be represented by a "sublimation" curve, all points above the curve corresponding to the existence of solid only, and all points below the curve to the existence of vapour only.

These three curves necessarily have a common point of intersection; in as much as the closed area produced by their meeting otherwise, would correspond to the existence of each form of matter by itself to the

FIG. 1 TRIPLE-POINT CURVES
(Schematic)


Solid
Liquid
Vapour
(Melting-point Curve)
Melting-point Curve
Boiling-point Curve
Sublimation Curve
3
Pressure
Temperature

exclusion of the other two forms; obviously a contradictory and impossible conclusion. The common intersection of these three curves is termed the "triple point", 3.

If a substance expands on solidification its melting curve slopes upward to the left as is shown by the dotted line in Fig. 1. It will be noticed that a substance which contracts on solidifying can not exist as liquid at temperatures below that of the triple point, but that it can be solidified by adequate pressure at higher temperatures. A substance which expands on solidifying can not be solidified at temperatures above that of the critical point, no matter how great the pressure, but can exist as solid, liquid and vapour at lower temperatures.

3. Pressure - Volume Relations for the States of Matter

A. Isothermal Curves

Curves showing the experimentally obtained relations between the pressure and volume of a mass of gas for constant temperatures may be plotted in these three dimensions, but commonly the perpendicular projections of these curves upon the pressure - volume plane, the isothermal curves of Fig. 2, are used. This figure represents graphically the results of Andrews' famous researches on carbon dioxide at temperatures from 13 to 48 degrees centigrade, and is a typical case. At the higher temperatures the isothermals approximate rectangular hyperbolas, but depart from this type of curve as the temperature diminishes, and show discontinuities limiting a horizontal portion of increasing length at temperatures below 30.92 degrees centigrade, the critical temperature for this gas.

The left-hand area shown in Fig. 2 corresponds to the existence of liquid only; the somewhat dome-shaped area to that of saturated

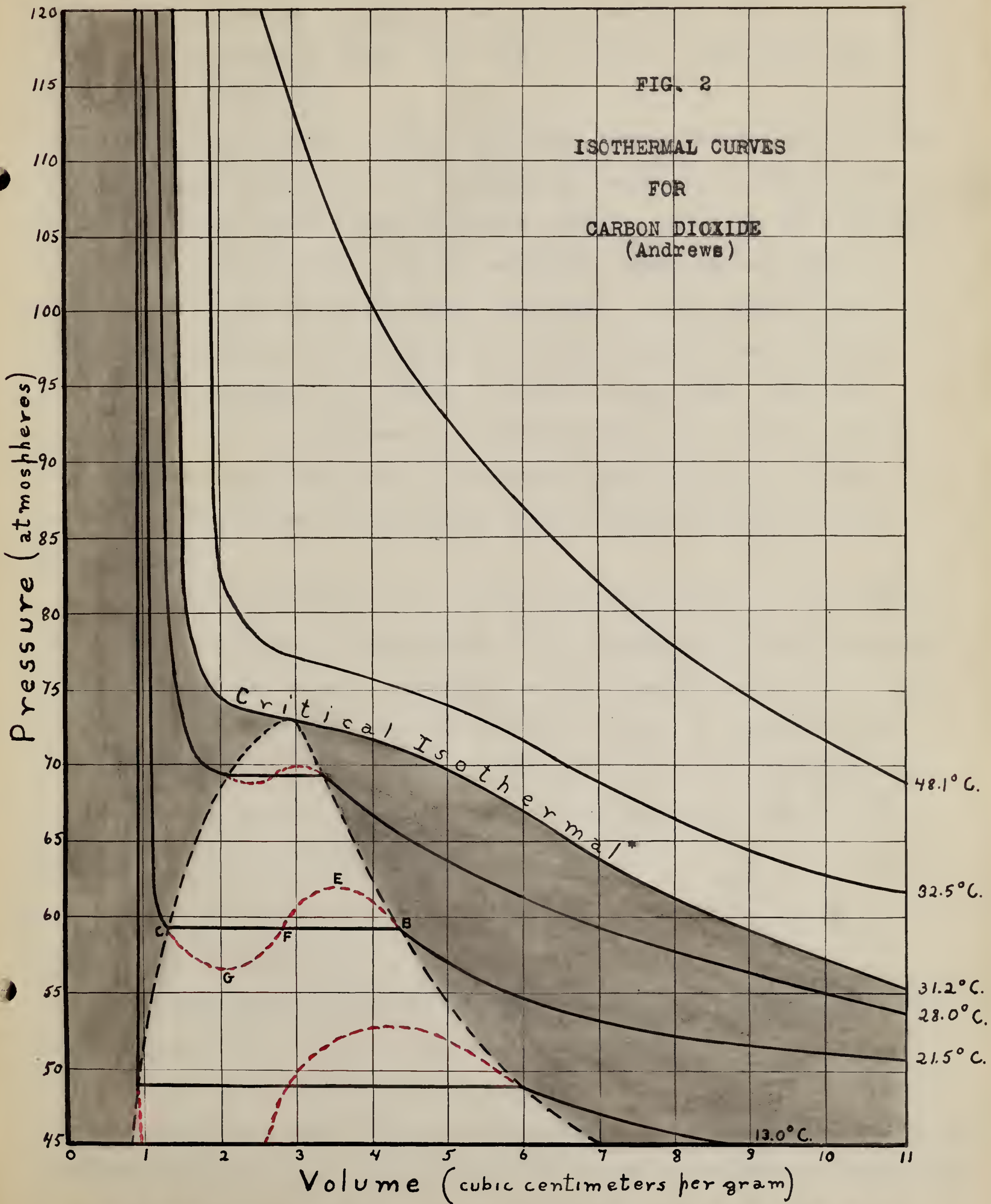


FIG. 2

ISOTHERMAL CURVES

FOR

CARBON DIOXIDE
(Andrews)

*Approximate only, as true critical isothermal is that of 30.92°C.

vapour in the presence of liquid; the area downward to the right to the presence of unsaturated vapour only; and the upper, right-hand area to the presence of gas only.

Following along the critical isothermal from right to left, we find that increasing pressure on the confined saturated vapour causes diminution in volume, which means increasing density, until at the critical point the volume and density of the saturated vapour become equal to those of the liquid under the same conditions. At this point vapour merges into liquid, and the latter is distinguishable from the former only by the appearance of a definite surface or meniscus. The horizontal portion of an isothermal, proceeding from right to left, represents progressive liquefaction of saturated vapour with no increase of pressure as the volume is diminished, until all the saturated vapour has condensed.

The critical constants of a substance may be defined in the following terms. The critical temperature is the highest temperature at which liquefaction of the gaseous substance can be effected by pressure. The critical pressure is that required to cause the gas to liquefy at the critical temperature. The critical volume is that of the gas or liquid at the critical point. Similarly the critical density is that of the gas or liquid at the critical point.

B.Isothermal-Curve Equations

a.Inadequacy of Boyle's Law

The mathematical expression of Boyle's Law, $P\ V = \text{constant}$ (for constant temperature), is obviously inadequate to express the pressure-volume relationship depicted by the isothermal curves in Fig. 2, excepting possibly in the cases of very low pressures and very high temperatures, when the isothermals have approximately the form of rectangular hyperbolas.

Claude* points out that "non-saturated vapours depart from Marriotte's (Boyle's) Law the closer they approach saturation."

Amagat** found that in general the P V products of a given mass of gas do not have a constant value but show a tendency to increase for very low and for very high pressures, having a minimum value for a definite intermediate value of pressure. Hydrogen did not show an intermediate minimum value for the P V product but instead a continual increase in its value with increasing pressure. Because of this apparently exceptional behavior hydrogen was termed a "more than perfect" gas.

b. James Thomson's Hypothesis

James Thomson offered a most helpful suggestion relative to the form of the isothermal curves below the critical temperature. He suspected that physical transformations are essentially continuous, and that consequently the discontinuity of the isothermals below the critical point is apparent only. He reasoned from the shape of the isothermal at the critical point that, below it, the curves could be expected to take the sinuous form shown by the red lines in Fig. 2.

He explained that this part of the curve probably could not be realized in practice as it represents unstable states of matter. Those portions similar to C G correspond to the condition of superheating; those similar to G E, to sudden vaporization as "bumping"; those similar to B E, to supersaturation; and those similar to E F, to a sudden condensation. Very careful manipulation has made it possible to obtain, experimentally, portions of the theoretical isothermals similar to C G and B E.

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* Claude, Liquid Air, p.15

** Amagat, Memoir in "Laws of Gases" by Barus p.53

Clerk Maxwell showed that the areas above and below the horizontal line, as C G F and F E B, are necessarily equal although not necessarily of the same shape.

c.Van der Waals' Equation

The mathematical statement of Boyle's Law, which has already been given as $\left[P\ V = \text{const.} \right]_{t\,=\,\text{const.}}$ can advantageously be expressed as $P\ V = R\ T$, wherein R is a constant for the given conditions, and T is the absolute temperature of the gas. It has been pointed out that an equation of this type is inadequate to express the isothermal curves. Stimulated by the suggestion of Thomson's just referred to, Van der Waals modified Boyle's Law by allowing: (1) for the attractions of neighboring molecules of the gas, and (2) for the finite dimensions of the molecules.

He postulated that the observed pressure, P, on a confined gas is less than the actual pressure, due to unbalanced molecular attraction upon the molecules near the confines of the gas, by an amount directly proportional to the square of the density of the gas, which he expressed as $\frac{a}{V^2}$ wherein (a) is a constant and V is the volume of the gas, thus making the expression for full pressure $(P - \frac{a}{V^2})$. He considered that, due to the finite size of the gas molecules, the observed volume, V, is greater than the true volume; so he corrected the observed volume by subtracting from it a constant, making the expression for volume $(V - b)$.

Van der Waals' equation is then $(P - \frac{a}{V^2})(V - b) = R\ T$. This equation plotted graphically gives curves similar in form to those obtained by Andrews above the critical temperature and to those suggested by Thomson for temperatures below it.

Solution of the Van der Waals equation as a cubic in V gives three roots equal at the critical point, resulting in the following expressions

for critical volume, pressure and temperature in terms of the constants: $V_c = 3b$, $P_c = \frac{a}{27b^2}$ and $T_c = \frac{8a}{27Rb}$. Substituting in this expression for critical temperature, constants obtained from Regnault's data on the compression of carbon dioxide, Van der Waals obtained a value for the critical temperature of that gas within two percent of the value obtained experimentally by Andrews.

Van der Waals' equation may be put in a general form independent of constants for any particular gas, a, b, and R, by expressing V, P, and T as fractions of the corresponding critical values, giving the equation, $(\lambda + \frac{3}{\mu^2})(3\mu - 1) = 8\nu$, in which $\lambda = \frac{P}{P_c}$, $\mu = \frac{V}{V_c}$, and $\nu = \frac{T}{T_c}$.

It must be noted that Van der Waals' equation, although most helpful, does not accurately represent conditions for all substances, and hence can not be considered a correct statement, but rather as a reasonably close approximation. The equation is also unsatisfactory in that it does not give an explanation of solidification, which an isothermal curve might be expected to do, considering this change of state a stage in a continuous physical process.

4. Conditions Necessary for the Liquefaction and Solidification of Gases

A. Temperature and B. Pressure

The work of Andrews made clear the existence of a limiting temperature above which a gas can not by any means be liquefied, the critical temperature which has been discussed. The early condensations of gases were successful because the working temperature was below the critical temperature of the gas. At that time it was noticed that the pressure required for condensation diminished as the temperature was lowered. Nevertheless, subsequent experiments greatly magnified the importance of pressure and neglected the matter of reducing the temperature, probably partly because it seemed then easier to increase pressure than to lower temperature. We know now, that high pressures are not needed if the

gas is well below its critical temperature; in fact, many gases liquefy at atmospheric pressure merely on being sufficiently cooled.

The problem of solidifying gases which have been liquefied involves cooling them below their respective triple-points, and has not been particularly difficult excepting in the case of helium which required a very low temperature. In most instances the pressure required for solidification is very moderate, atmospheric pressure often sufficing. Indeed, in case a liquid expands on solidifying, an increase of pressure on the cooled liquid serves to delay or even to prevent solidification. Frequently, cooling the liquefied gas a few degrees will cause it to congeal.

C. Difficulties with the So-called "Permanent" Gases

As late as 1877 some gases were termed "permanent" because they had resisted all attempts to liquefy them. In the case of these gases the experimenters had not cooled them to or below their critical temperatures, and consequently even excessively high pressures proved of no avail. When attention was directed to the matter of producing lower and lower temperatures, one after another of the "permanent" gases was condensed, on being compressed when cooled below its critical temperature. The problem of lowering the temperature became increasingly difficult because the rate of heat influx from the surroundings to the gas being cooled, increases as the temperature falls, and the critical temperature of helium proved to be -268.5 degrees centigrade or only 4.6 degrees above absolute zero! Along with the matter of lowering the temperature, experimenters had to consider the matter of insulating the cooled gas against outside heat, as will be described later.

D. Van der Waals' Criteria for Change of State

Using the symbols: T_c, T_3 and T for the critical, triple-point and

obtained temperatures respectively, Van der Waals* states that if a gas is to liquefy, the following condition must be satisfied, $T_c > T > T_3$. If solidification is to occur, $T_c > T < T_3$. Thus a substance is a gas above T_c, condensible between T_c and T_3, and a solid below T_3, if super-cooling is not considered. The highest pressure for condensation occurs at T_c, the lowest at T_3. This pressure of the triple point is usually less than one atmosphere. If the ratio of T_c to T_3 is large, then the pressure of the triple point is likely to exceed one atmosphere.

Most substances have T_c above ordinary temperatures, T_o, and so will condense under pressure at ordinary temperatures. If $T_c > \frac{5}{3} T$, the substance occurs as a liquid at ordinary temperatures. Methane, nitrous oxide, oxygen, carbon dioxide, nitrogen, hydrogen and the rare gases all have $T_c < 0^\circ$ C. and so can exist only as gases at ordinary temperatures.

5. Methods of Compression

In most of the earlier liquefactions of gases the compression of the gas was secured by continued evolution of gas by chemical action in a confined space. This method permitted very high pressures but often resulted in dangerous explosions. Faraday used this method in his earlier work.

Another method, which gave very high yet safe pressures, made use of the facts: (1) that the volume expansion of liquids is much greater than that of solids, and (2) that liquids are practically incompressible. Berthelot liquefied several gases confined above mercury by the pressure obtained by the expansion of that liquid by heat. In this way he obtained pressures as high as 780 atmospheres.

Several investigators applied pressure to gases by means of hydraulic presses of the screw type. The gas was confined above a liquid,

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* Encyclopaedia Britannica, 12 Ed., Vol.6, p.844

usually mercury, and the desired pressure applied to the mercury, or to another liquid in contact with it, by the slow advance of a screw plunger of large mechanical advantage into the cylinder of liquid. Andrews' apparatus was of this type.

Other experimenters made use of reciprocating pumps to obtain the pressure on the gas. The earlier devices of this type were hand operated, and frequently did not pump the gas itself, but pumped a liquid into a chamber below the gas. Natterer's pump, having a small cylinder and short stroke, produced extremely high pressures on the gas directly.

Later compression pumps were engine driven, some compressing the gas directly, and others pumping liquids such as water. Cailletet's pump was of the latter type. More-recent compressors have been of the multistage type, having two or more cylinders, each raising the pressure of the gas delivered to it, and each, excepting the last, delivering the compressed gas to a higher-pressure cylinder. Such machines have large capacity, produce high pressures, and require water-cooling to remove the heat of compression from the gas.

6. Methods of Cooling

A. By Auxiliary Liquids

a. Heat-absorbing Mixtures

Aside from experimenting out-of-doors or in unheated rooms in the winter, early investigators in this field relied upon heat-absorbing mixtures to produce low temperatures. A mixture of ice and water gives a steady temperature of 0 degrees centigrade, the heat absorbed from the gas being cooled going to melt the ice. A mixture of salt and ice gives a temperature as low as -21.3 degrees centigrade, and a certain mixture of crystallized calcium chloride and ice gives a temperature of -54.9 degrees centigrade. "Thilorier's Mixture" of carbon dioxide-snow

and ether gives -77 degrees centigrade under atmospheric pressure, and as low as -110 degrees centigrade under exhaustion.

b. Cold Liquids

With the production of liquid gases, new refrigerants were available. Liquid gases behave like free-boiling water, in that after a certain boiling temperature is reached, any influx of heat does not increase the temperature, but merely causes some of the liquid to boil away. The boiling-points of most gases are well below ordinary temperatures, so that surrounding the gas under investigation with a liquefied gas, gives a steady low temperature.

c. Rapid Evaporation of Liquid Gases

In as much as the boiling temperature varies with the pressure upon the liquid, it was found that the boiling-point of liquid gas could be decidedly lowered by allowing it to boil "in vacuo". The temperature falls until it reaches the point at which the vapor pressure of the liquid is equal to the pressure upon it. Moreover, lowering the temperature causes the heat of vaporization of the liquid gas to increase (from zero at the critical temperature), thus increasing the heat-absorbing power of the refrigerant. Expressed in degrees centigrade, the temperatures given by various liquid gases under exhaustion are approximately: carbon dioxide -130, oxygen -194, nitrogen -211, hydrogen -256, helium -272.

d. Cascade Method

Van der Waals* states that, using a liquid gas at greatly reduced pressure as a cooling bath, the lowest temperature practically obtainable is that of the triple point, T_3, for that substance. By using as a refrigerant a liquid gas having a T_c considerably above that of the gas

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* Encyclopaedia Britannica, 12th Ed., Vol.6, p.848

which it is desired to condense, and having a T_3 considerably below the T_c of this latter gas, it is possible by means of the boiling of the liquid gas "in vacuo" to cool the other gas enough to permit liquefaction. This liquefied gas can in turn be used to produce a temperature as low as its T_3. Thus a series of refrigerating stages can be built up and very low temperatures attained.

If the ratio of T_c of the refrigerant gas to the T_c of the gas to be liquefied is much greater than 2, the series fails as the T_3 of the refrigerant is either above or too little below the T_c of the other gas. This accounts for the failure of nitrogen as a refrigerant in attempts to liquefy hydrogen, the T_c of which proved to be lower than the T_3 of nitrogen.

The method which has been outlined is termed the "cascade method". It requires complicated apparatus and close attention; but gives a constant low temperature, and permits wide regulation of temperature. One series of refrigerants which has been much used at the Cryogenic Laboratory at Leyden consists of methyl chloride, ethylene and oxygen in successive stages.

B. By Adiabatic Expansion

When a highly compressed gas is allowed to expand under such conditions that heat inflow or outflow is prevented, it is found that the temperature of the gas falls, largely because of the work done by the gas in pushing back the atmosphere at the expense of the heat content of the gas. This was the first method by which some of the so-called "permanent" gases were liquefied. The highly compressed gases, cooled as much as possible by auxiliary refrigerants, experienced a sufficient fall in temperature on expanding to produce condensation in fine drops. Cailletet used this method successfully on oxygen, nitrogen and air.

a. Joule-Thomson Effect

These investigators allowed compressed gases to expand adiabatically through a porous plug into a vacuum, taking the temperature of the gas before and after expansion. For most gases they found a fall in temperature, but for hydrogen a slight increase of temperature.* Subsequent investigators have shown that the Joule-Thomson effect changes with the temperature of the gas, and that each gas has its point of inversion of the effect, that is, a change from a cooling to a heating effect at a sufficiently high temperature. Ewing** states, "For any gas there is, in fact, a particular temperature below which the effect of throttling is to cool the gas, and above which the effect of throttling is to heat it."

Hydrogen precooled to 192.5 degrees absolute cools upon expanding like other gases. This cooling effect results from the internal work done as the molecules of the gas increase the intermolecular distances against the forces of attraction between neighboring molecules.

C. By Regenerative Methods.

a. Unbalanced- expansion

The cooling effect of the expansion of gases at temperatures below the inversion point is small, but its value increases with difference of pressure and with decrease of temperature. Dickson*** gives the fall in temperature in centigrade degrees as $0.276\,(p_2 - p_1)\left(\frac{273}{T}\right)$ wherein T is the initial absolute temperature of the gas and p_2 and p_1 are the pressures in atmospheres before and after expansion.

This method has been adapted to continuous regenerative processes in which cooled expanded gas cools compressed gas about to expand, making

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* Thomson and Joule, Memoir in "Free Expansion of Gases" by Ames, pp.30-103

** Ewing, Mechanical Production of Cold, p.144

*** Dickson, Industrial Gases by Martin, p.4

possible a still lower temperature for this gas after expansion. As the process continues, the temperature of the expanding gas falls below the critical point, and liquefaction occurs. Onnes made use of this method to cool helium below its critical temperature for the first time. Linde's liquid-air machines employ this method.

b. Balanced-expansion

In gas-liquefying machines of the Claude type* the Joule-Thomson cooling effect is supplemented by causing the expanding gas to perform external work in running a reciprocating type of engine under load, thus reducing the heat content of the gas by conversion into mechanical energy, and consequently, lowering the temperature of the gas. The use of the engine is primarily not to secure power but to lower the temperature of the gas by reducing its heat content.

In the balanced-expansion type of liquefier the gas does both internal and external work on expanding, so this type of machine is more efficient than the unbalanced-expansion type.

7. Methods of Heat Insulation

As the temperature of a substance is lowered below that of its surroundings, heat tends to flow into the substance from them. The rate of heat-inflow increases with difference of temperatures, consequently the colder a gas becomes, the more difficult it is to keep it cold.

A. Packing

The critical temperatures of the gases liquefied by the earlier experimenters were not greatly below ordinary temperatures, so they obtained sufficient heat insulation for the cooling baths and for the gases by simple packing with very poor conductors of heat. For example

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* Ibid, p.5

Faraday* in his second series of liquefactions used as a container for the cooling bath, (Thilorier's Mixture), a double dish with dry flannel between. Elaborations of this method were used by various experimenters until the introduction of the vacuum vessel in 1893.

B. Dewar or Vacuum Flasks

Dewar constructed a double-walled bulb of glass, which is a poor conductor of heat, and produced as high a vacuum as possible between the walls. Exhausting this interspace, thus removing most of the molecules of air, greatly reduces within it the conductive and the convective transfer of heat from the atmosphere to the contents of the bulb, but does not diminish heat inflow by radiation, however.

By silvering the surface of the interspace, heat transfer by this last-mentioned method is greatly cut down in that the shiny surface of the outer wall acts as a very poor radiator, while the shiny surface of the inner wall acts as a very good reflector of radiant heat. So it is evident that the vacuum flask cuts down to almost negligible values the heat inflow by the three possible processes of conduction, convection and radiation.

In loosely stoppered containers of this type holding a liter or more liquid air can be kept without serious loss for several days, whereas it would entirely evaporate from an ordinary vessel in a few hours at most. It has already been mentioned that Keesom employed several vacuum flasks one within the other in the solidification of helium.

C. Influence of the Spheroidal State

Sloane** considers that liquid gases assume the spheroidal state, and consequently, are separated from their containers by a thin gas-space which is a poor conductor of heat. Such a condition would doubtless

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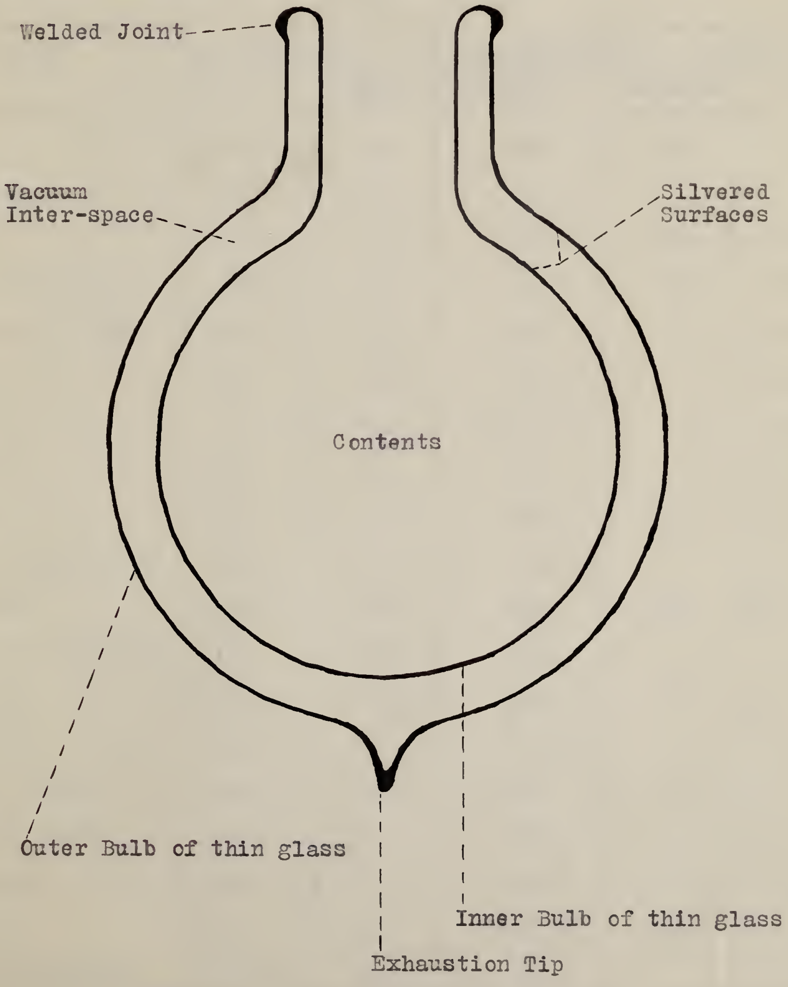
* Faraday, Liquefaction of Gases, p.35

** Sloane, Liquid Air and the Liquefaction of Gases

FIG. 3 DEWAR FLASK in Vertical Section


Welded Joint
Vacuum Inter-space
Silvered Surfaces
Contents
Outer Bulb of thin glass
Inner Bulb of thin glass
Exhaustion Tip

help greatly in retarding the inflow of heat to a liquid gas, and thereby permit it to remain liquid for a longer time than if it were in actual direct contact with its container.

8. Critical and Other Constants for Various Gases

NAME	CRITICAL		BOILING-POINT C.		MELTING-POINT C.
	Temp. C.	Pressure atmos.	Atmospheric Pressure	Reduced Pressure	
Air	-140	39	-192	-205	. . .
Ammonia	130	115.0	-38.5	. . .	-77
Argon	-117.4	52.9	-186.2	-194.2	-188
Carbon Dioxide	30.92	73	-78.2	-130	-57
Carbon Monoxide	-141.1	35.9	-190	. . .	-207
Chlorine	146	93.5	-33.6	. . .	-101.5
Ethylene	10	51.7	-102.7	. . .	-169
Fluorine	-120	40	-187	. . .	-223
Helium	-268	2.3	-268.5	-272	-272
Hydrochloric Acid	52.3	86	-83.1	. . .	-112.5
Hydrogen	-234.5	20	-252	-256	-259
Hydrogen Sulphide	100	88.7	-61.8	. . .	-85.5
Krypton	-62.5	54.3	-151.7	. . .	-169
Methane	-95.5	50	-1.5	. . .	-84
Nitric Oxide	-93.5	71.2	-153	. . .	-160.6
Nitrous Oxide	38.3	77.5	-89.4	. . .	-102.4
Nitrogen	-146	33	-195.8	-210.6	-210.5
Oxygen	-118	50	-182.7	-194	-218
Sulphur Dioxide	155.4	78.9	-10	. . .	-72.7

SUMMARY OF PART I

THE MORE IMPORTANT STEPS IN THE HISTORY OF THE EXPERIMENTAL LIQUEFACTION AND SOLIDIFICATION OF GASES

Lavoisier, Dalton and other scientists appreciated the possibility of condensing gases.

Monget and Clouet, by compression and cooling, condensed sulphurous acid gas before 1800.

Northmore, in 1805, by compression, liquefied chlorine, hydrochloric acid gas and sulphurous acid gas.

La Tour, in 1822, developed the idea that at a certain temperature a liquid and its vapour have the same density.

Faraday, in 1823, began a series of liquefactions of the less difficult gases, obtaining pressure by confined chemical action, and cooling the compressed gas.

Thilorier, in 1834, liquefied carbon dioxide in like manner in considerable quantities, and developed the cooling bath known as "Thilorier's Mixture."

Natterer, in 1844, liquefied carbon dioxide and nitrous oxide by cooling the gas which had been highly compressed by a pump.

Faraday, in 1845, began another series of liquefactions, employing mechanical compression with cooling. He condensed seven gases and also solidified seven.

Berthelot, in 1850, liquefied several gases by the pressure produced by the thermal expansion of mercury.

Andrews, in 1863, by his work on carbon dioxide, developed the concept of a critical temperature above which a gas can not be liquefied.

Cailletet, in 1877, condensed several gases, among them oxygen, carbon monoxide, nitrogen and air, by adiabatic expansion of the highly

compressed and cooled gas.

Pictet, in 1877, by adiabatic expansion of the compressed gas cooled by the cascade method, liquefied and solidified oxygen and hydrogen.

Hautefeuille and Chappuis, in 1882, liquefied ozone.

Wroblewski and Olszewski, in 1883, by strong compression and cooling, liquefied several of the so-called "permanent" gases.

By evaporating the liquid gases under reduced pressure Olszewski solidified a number of gases.

Linde invented the unbalanced-regenerative expansion method of cooling gases, which is a continuous process adaptable to large scale production.

Dewar developed several machines for liquefying gases. He liquefied several of the more difficult gases including hydrogen. He invented the vacuum bottle for storing liquid gases. In 1897, Moissan and Dewar liquefied fluorine.

Olezewski, in 1895, liquefied and solidified argon by pressure and cooling.

Ramsay and Travers, in 1898, liquefied neon, krypton and xenon at low temperatures.

Rutherford and Soddy, in 1902, condensed thorium emanation; Whytlaw-Gray and Ramsay liquefied and solidified niton.

Kamerlingh-Onnes, in 1908, working at very low temperatures, liquefied helium.

With the solidification of helium by Keesom in 1926, all known gases have been liquefied and solidified.

SUMMARY OF PART II

THEORY AND PRACTICE IN THE LIQUEFACTION AND SOLIDIFICATION OF GASES

Matter occurs as solids or fluids. Fluids include liquids, vapours and gases. The states of matter are characterized by different intensities of molecular motion. All molecular motion ceases at the absolute zero of temperature.

The pressure-temperature relations for the different phases of matter may be represented by melting-point, boiling-point and sublimation curves; all of which have a common point of intersection, the triple point.

An isothermal curve shows the pressure-volume relations of the different phases of a substance for a given temperature. Liquefaction of a gas is not possible above a certain temperature, the critical temperature for that gas. Other critical constants are recognized.

Boyle's Law is inadequate to express the isothermal curves except well above the critical point. Thomson suggested that the true form of the apparently discontinuous portion of the isothermal curve might well be sinuous.

Van der Waals corrected Boyle's Law by allowing for the attractions of neighboring molecules. His equation, while a fair approximation, is not exact.

To liquefy a gas, it must be cooled below its critical temperature, and also adequately compressed. The pressure required for liquefaction is moderate for temperatures well below that of the critical point. The so-called "permanent" gases have unusually low critical temperatures which are increasingly difficult of attainment. Liquid gases solidify under moderate pressure when cooled below their triple-points.

Gases may be compressed by various devices: confined chemical

action, thermal expansion of a liquid, hydraulic screw-type presses, hand-driven reciprocating pumps, and single- and multi-stage engine-driven pumps.

Methods by which gases may be cooled are: by heat-absorbing mixtures, by cold liquids, by rapid evaporation of liquid gases, by unbalanced- and balanced-expansion each regeneratively applied.

Cold substances may be fairly well insulated against inflow of heat from their surroundings by simple packing with poor conductors, and much more effectively insulated by vacuum flasks as containers.

A thin gas-space between the liquid gas and the container would help to diminish heat inflow.

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